

# DESIGN OF MOLECULAR MATERIALS FOR NON-LINEAR OPTICS BASED ON ALKAPLANES AND FENESTRANES DONOR GROUPS

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We have investigated the spectroscopic and non-linear optical (NLO) properties of hydrocarbons containing (quasi-)planar tetracoordinated carbon atoms, particularly, fenestranes<sup>1</sup> and alkaplanes<sup>2</sup>. These compounds are well known for their low ionization energies (IE). Thus, they can be used as donors in Acceptor-Bridge-Donor (A-B-D) systems. Structures and vibrational frequencies were performed at B3LYP, MP2 and CCSD levels with 6-311+G(2d,p) basis sets. Static polarizabilities ( $\alpha$ ) and first hyperpolarizabilities ( $\beta$ ) were calculated at the PBE1PBE/6-311G(d,p) level. Isotropic shieldings were calculated at the B3LYP/aug-pcS-2 level for the (quasi-)planar carbon atoms and at the B3LYP/6-311G(d,p) level for the other atoms.

Table 1. Influence of the ionization energies of the donor systems due to amine groups

	Donor	B3LYP/6-311+G(d,p)		MP2/6-311+G(2d,p)		CCSD/6-311+G(2d,p)	
		IE (eV)	$\nu_1$ (cm <sup>-1</sup> )	IE (eV)	$\nu_1$ (cm <sup>-1</sup> )	IE (eV)	$\nu_1$ (cm <sup>-1</sup> )
I	[5.5.5.5] fenestrahexene	6.53	122	6.68	122	6.92	122
II	[5.5.5.5]-tetraamine-fenestrahexene	5.33	64	5.63	66	-	-

According to the Table 1, the presence of amine groups decreases more than 1 eV the IE, probably by withdrawing electron density from the central ring. When these systems are connected to diethenylsilane (III)<sup>3</sup> and polienic-mesoionic (IV) bridges<sup>4</sup>; and tricyanovinyl (V) and nitrobenzyl (VI) acceptors, we have potential molecular materials for non-linear optics. In Table 2, we present the values of  $\alpha$  and  $\beta$  for systems based on donors I and II. The diethenylsilane (III) bridge is more efficient than the polienic-mesoionic (IV) ones. In addition, the smaller IE of Donor II compared to the Donor I leads to larger values for  $\alpha$  and  $\beta$ . The isotropic shieldings of the central carbon atom (C1) of fenestranes and its neighboring atoms (C2, C3, C4 and C5) are correlated to the dihedral angle ( $\omega_{\text{donor}}$ ) of the (quasi-)planar carbon.

Table 2. Static polarizabilities ( $\alpha$ ) and first hyperpolarizabilities ( $\beta$ ) for some A-B-D systems.

A	B	D	$\alpha_{\text{avg}}$ (10 <sup>-25</sup> cm <sup>3</sup> )	$\beta_{\text{mol}}$ (10 <sup>-30</sup> cm <sup>5</sup> esu <sup>-1</sup> )	Isotropic shielding (ppm)					$\omega_{\text{donor}}$ (°)
					C1	C2	C3	C4	C5	
V	III	I	5033	48480	65	-3	-8	3	-10	24.5
V	IV	II	2133	3294	79	43	4	27	10	26.4
VI	IV	II	2348	5148	79	44	2	23	15	26.2
VI	III	II	5062	56831	70	30	4	30	6	25.6
V	III	II	16699	120002	70	30	6	31	6	25.6

We conclude these molecular materials based on donor groups and diethenylsilane bridge are potential candidates for non-linear optics applications since they have the largest values of  $\alpha$  and  $\beta$  reported<sup>3,4</sup>. Also, these molecular materials allow fine control of isotropic shielding and other molecular properties by the planarity of the central carbon in the donor group.

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